

Application No. 10/695,015  
Amendment dated March 14, 2006  
Reply to Office Action of December 14, 2005

Docket No.: PI 1330 USNA

#### AMENDMENTS TO THE SPECIFICATION

Please replace the paragraph beginning at page 1, line 5, which starts with "The invention relates to" with the following amended paragraph:

The invention relates to the hydrocyanation of either 2-pentenitrile, 3-pentenitrile, 4-pentenitrile, 2-methyl-3-butenitrile, or mixtures thereof to produce adiponitrile (ADN) and/or 2-methylglutaronitrile (MGN) using a ~~zero-valent~~ zero-valent nickel catalyst promoted by a byproduct of the chlorination of titanium-rich ores.

Please replace the paragraph beginning at page 1, line 10, which starts with "US Patent 3,496,217 issued" with the following amended paragraph:

~~US Patent~~ U.S. Pat. No. 3,496,217, issued in 1970, discloses an improvement in hydrocyanation using a large number of metal cation compounds with a variety of anions as catalyst promoters. ~~US Patent~~ U.S. Pat. No. 3,925,445, issued in 1975, discloses ~~zero-valent~~ zero-valent nickel hydrocyanation catalysts promoted with metal halides and organoboron compounds. ~~US Patent~~ U.S. Pat. No. 4,774,353, issued in 1988, discloses ~~zero-valent~~ zero-valent nickel hydrocyanation catalysts promoted with triorganotin compounds. ~~US Patent~~ U.S. Pat. No. 4,874,884, issued in 1989, discloses ~~zero-valent~~ zero-valent hydrocyanation catalysts promoted using a synergistic combination of promoters. ~~US Patent~~ U.S. Pat. No. 6,048,996, issued in 2000, discloses ~~zero-valent~~ zero-valent hydrocyanation catalysts promoted using an insoluble Lewis acid promoter.

Please replace the paragraph beginning at page 1, line 22, which starts with "The present invention provides" with the following amended paragraph:

The present invention provides a process for the preparation of adiponitrile by the addition of hydrogen cyanide to either 2-pentenitrile, 3-pentenitrile, 4-pentenitrile, or mixtures thereof in the presence of a ~~zero-valent~~ zero-valent nickel catalyst, and a promoter

Application No. 10/695,015  
 Amendment dated March 14, 2006  
 Reply to Office Action of December 14, 2005

Docket No.: PI 1330 USNA

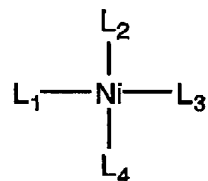
obtained as a byproduct from the chlorination of titanium-rich ores. This byproduct comprises iron (II) chloride and manganese (II) chloride. The crude byproduct can be used directly in the hydrocyanation reaction without separation steps.

Please replace the paragraph beginning at page 1, line 29, which starts with "The present invention also" with the following amended paragraph:

The present invention also provides a process for the preparation of 2-methylglutaronitrile by the addition of hydrogen cyanide to 2-methyl-3-butenitrile in the presence of a ~~zerovalent~~ zero-valent nickel catalyst, and a promoter obtained as a byproduct from the chlorination of titanium-rich ores, comprising iron (II) chloride and manganese (II) chloride.

Please replace the paragraph beginning at page 3, line 3, which starts with "A preferred group" with the following amended paragraph:

A preferred group of these Ni(0) catalysts have the general structure:



wherein L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>, and L<sub>4</sub> are neutral ligands which may be the same or different and have the formula P(XYW) wherein X and Y are selected from the group consisting of R and OR', and W is OR'', wherein R, R', and R'' may be the same or different, and wherein R, R', and R'' are selected from the group consisting of alkyl and aryl groups containing up to 18 carbon atoms, with aryl being preferred. Alkyl groups may be linear or branched. A particularly preferred group within the foregoing ~~zerovalent~~ zero-valent nickel catalysts is that disclosed in U.S. Patent Pat. No. 3,903,120. This preferred group of catalysts can be described by the general formula NiL<sub>4</sub>, where L is a neutral ligand such as a triarylphosphite of the formula P(OAr)<sub>3</sub>, wherein Ar is an aryl group of up to 18 carbon atoms. Illustrative of the aryl groups are

Application No. 10/695,015  
 Amendment dated March 14, 2006  
 Reply to Office Action of December 14, 2005

Docket No.: PI 1330 USNA

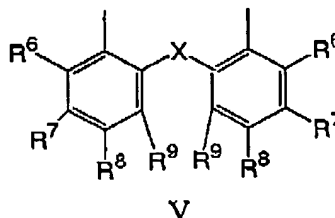
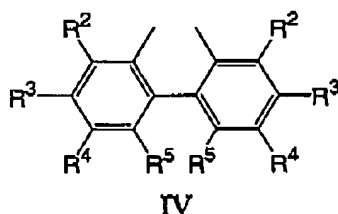
methoxyphenyl, tolyl, xylyl, and phenyl. Preferred aryl groups are meta-tolyl, para-tolyl, and phenyl, and mixtures thereof.

Please replace the paragraph beginning at page 3, line 19, which starts with "Suitable ligands for" with the following amended paragraph:

Suitable ligands for the present invention are also bidentate phosphorous-containing ligands selected from the group consisting of bidentate phosphites, and bidentate phosphinites. Preferred ligands are bidentate phosphite ligands.

Please replace the paragraph beginning at page 4, line 1, which starts with "In formulae I, II, and III" with the following amended paragraph:

In formulae I, II, and III,  $R^1$  is phenyl, unsubstituted or substituted with one or more  $C_1$  to  $C_{12}$  alkyl or  $C_1$  to  $C_{12}$  alkoxy groups; or naphthyl, unsubstituted or substituted with one or more  $C_1$  to  $C_{12}$  alkyl or  $C_1$  to  $C_{12}$  alkoxy groups; and Z and  $Z^1$  are independently selected from the group consisting of structural formulae IV, V, VI, VII, and VIII:



wherein:

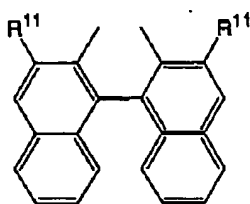
$R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$ , and  $R^9$  are independently selected from H,  $C_1$  to  $C_{12}$  alkyl, and  $C_1$  to  $C_{12}$  alkoxy;

X is O, S, or  $CH(R^{10})$ ;

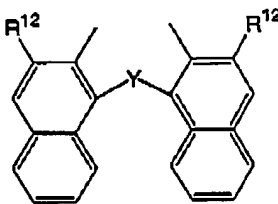
$R^{10}$  is H or  $C_1$  to  $C_{12}$  alkyl;

Application No. 10/695,015  
 Amendment dated March 14, 2006  
 Reply to Office Action of December 14, 2005

Docket No.: PI 1330 USNA



VI



VII

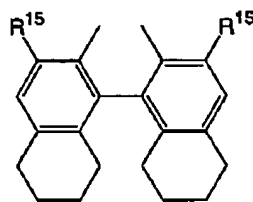
wherein:

$R^{11}$  and  $R^{12}$  are independently selected from H,  $C_1$  to  $C_{12}$  alkyl, and  $C_1$  to  $C_{12}$  alkoxy[[]], and  $CO_2R^{13}$ ;

$R^{13}$  is  $C_1$  to  $C_{12}$  alkyl or  $C_6$  to  $C_{10}$  aryl, unsubstituted or substituted[[]] with  $C_1$  to  $C_4$  alkyl;

Y is O, S,  $CH(R^{14})$ ;

$R^{14}$  is H or  $C_1$  to  $C_{12}$  alkyl;



VIII

wherein:

$R^{15}$  is selected from H,  $C_1$  to  $C_{12}$  alkyl, and  $C_1$  to  $C_{12}$  alkoxy[[]], and  $CO_2R^{16}$ [[]];

$R^{16}$  is  $C_1$  to  $C_{12}$  alkyl or  $C_6$  to  $C_{10}$  aryl, unsubstituted or substituted with  $C_1$  to  $C_4$  alkyl.

Please replace the paragraph beginning at page 5, line 10, which starts with "In the structural formulae" with the following amended paragraph:

In the structural formulae I through VIII, the  $C_1$  to  $C_{12}$  alkyl[[]] and  $C_1$  to  $C_{12}$  alkoxy groups may be straight chains or branched.

Please replace the paragraph beginning at page 8, line 1, which starts with "Suitable bidentate phosphites" with the following amended paragraph:

Application No. 10/695,015  
Amendment dated March 14, 2006  
Reply to Office Action of December 14, 2005

Docket No.: PI 1330 USNA

Suitable bidentate phosphites are of the type disclosed in ~~U.S. Patents~~ U.S. Pat. Nos. 5,512,695; 5,512,696; 5,663,369; 5,688,986; 5,723,641; 5,847,191; 5,959,135; 6,120,700; 6,171,996; 6,171,997; and ~~6,399~~ 6,399,534. Suitable bidentate phosphinites are of the type disclosed in ~~U.S. Patents~~ U.S. Pat. Nos. 5,523,453 and ~~5,693~~ 5,693,843.

Please replace the paragraph beginning at page 8, line 9, which starts with "In the production of" with the following amended paragraph:

In the production of titanium tetrachloride, raw materials, including ilmenite or rutile ores or other titanium-rich materials such as those obtained from beneficiating these ores, are reacted with chlorine under reducing conditions to yield a mixture of metal chlorides from which titanium tetrachloride may be recovered. Iron chloride is present in the chlorination product of practically every case where iron-containing ores are used in the raw materials. Iron in the form of compounds or complexes is often present in titanium-containing materials that are chlorinated. Often such iron material will be present in an amount of about 0.5 to 50 percent by weight. A major amount of the iron material typically is present as iron oxide. The iron compounds in the titanium-containing material typically react to form iron chloride, which can be present in the form of ferrous chloride or ferric chloride. In addition, other metal chlorides, such as manganese or vanadium chloride, can be present in these mixtures to a smaller extent. A typical chlorination process is described in ~~US patent~~ U.S. Pat. No. 5,585,078.

Please replace the paragraph beginning at page 8, line 25, which starts with "In particular" with the following amended paragraph:

In particular, a process of chlorinating titanium-containing material in a fluidized bed reactor is known. Suitable processes are disclosed in ~~the following~~ U.S. ~~[[patents:]]~~ Pat. Nos. 2,701,179; 3,883,636; and 2,446,181. In such processes, particulate coke, particulate titanium-bearing material, chlorine and optionally oxygen or air are fed into a reaction chamber, and a suitable reaction ~~temperature~~ temperatures, ~~pressure~~ pressures and flow rates are maintained to sustain the fluidized bed. Gaseous titanium tetrachloride and other metal chlorides, such as iron-

Application No. 10/695,015  
Amendment dated March 14, 2006  
Reply to Office Action of December 14, 2005

Docket No.: PI 1330 USNA

based chlorides, are exhausted from the reactor chamber. The gaseous titanium tetrachloride so produced can then be separated, leaving behind a byproduct material that can be used as the promoter in the present invention.

Please replace the paragraph beginning at page 9, line 3, which starts with "Typical conditions and" with the following amended paragraph:

Typical conditions and specifications for fluidized beds useful for this invention are as follows: reaction temperature of about 900 to 1300°C, pressure of about 1.5 to 3 ~~atemspheres~~ atmospheres, reactor size of about 6 to 25 feet in diameter with multiple chlorine jets in or near the base, reactor superficial velocity of about 0.5 to 1.5 feet per second, and a settled bed depth of about 6 to 25 feet. Typically, the titanium-containing material initially fed has a particle size of about 70 to 800 microns in diameter, and the coke initially fed has a particle size of about 300 to 3000 microns in diameter. Preferably, the chlorine jets will be located within 0 to 10 feet of the base of the reactor.

Please replace the paragraph beginning at page 9, line 13, which starts with "The titanium-bearing material" with the following amended paragraph:

The titanium-bearing material can be any titanium source material, such as titanium-containing ores including rutile, ilmenite or anatase ore; beneficiates thereof; titanium containing by-products or slags; and mixtures thereof. Ordinarily, the titanium-bearing material contains iron oxide in an amount of about 0.5 to 50 percent by weight and preferably up to about 20 percent by weight.

Please replace the paragraph beginning at page 9, line 19, which starts with "A chlorination process" with the following amended paragraph:

A chlorination process that produces the byproduct promoter of this invention is the procedure described in U.S. ~~Patent~~ Pat. No. 4,961,911. A fluidized bed reactor can be operated

Page 7 of 12

Application No. 10/695,015  
Amendment dated March 14, 2006  
Reply to Office Action of December 14, 2005

Docket No.: PI 1330 USNA

at a temperature of 1000°C. This reactor is fed with an ore blend, containing approximately 74%  $\text{TiO}_2$   $\text{TiO}_2$  and 21.5% iron oxides and 4.5% other impurities, and with coke. A fluidizing gas is fed to a distributor at the bottom of the reactor and consists of about 75% chlorine and a diluent gas consisting primarily of nitrogen, hydrogen chloride, oxides of carbon and oxygen. The ore, coke and fluidizing gas are fed to the reactor at rates of 100 to 200 pounds per hour per square foot of reactor cross-sectional area, respectively. A stream of about 20 pounds of crude titanium tetrachloride per hour per square foot of reactor cross-sectional area is fed about 5 feet above the level of the static bed. The gases leaving the chlorinator contain the following typical components in the following typical percentages by volume: titanium tetrachloride 22%, iron chloride 7%, carbon dioxide 23%, carbon monoxide 3%, nitrogen 36 %, hydrogen chloride 7% and chlorine 0.03%. The off-gas titanium tetrachloride is directed to a cooling train and collected.

Please replace the paragraph beginning at page 11, line 4, which starts with "A typical byproduct promoter" with the following amended paragraph:

A typical byproduct promoter contains iron (II) chloride and smaller amounts of manganese (II) chloride and other by-product metal chlorides to a much smaller extent, in addition to other materials such as sand or coke. Some of the components of this byproduct promoter are not soluble in solvents for the hydrocyanation process or in mixtures of the substrate the nitriles. The byproduct promoter can be added to the hydrocyanation reaction mixture either directly as a solid; or as a slurry in either a hydrocyanation solvent or a mixture of nitriles; or as a homogeneous solution after filtration from materials which are not dissolved in the mixture of substrate nitriles or solvent. Typical methods of filtration applicable to the present invention are taught in Perry's Chemical Engineers' Handbook, McGraw-Hill Publishing Company.